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Effect of Lanthanum Doping on Modulating Thermochromic Properties of VO₂ Thin Films

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Lanthanum (La) doped vanadium dioxide (VO₂) thin films were fabricated through a facile sol-gel technique. The La doping was found to be effective in reducing the phase transition temperature (τ_c) of VO₂ below the 4 at.% doping level, with a reducing rate of -1.1 °C/at.%. In addition, below the 3 at.% La doping level, the band gap (E_g) decreased steadily with the increasing addition of La dopants. The 5 at.% La doping can enhance both integrated visible transmission (T_{lum}) and solar modulating ability (ΔT_{sol}) simultaneously. The combination of T_{lum} =50.1% and ΔT_{sol} =10.3% represents the best value for VO₂ continuous thin films.

Introduction

Vanadium dioxide (VO₂) is an interesting phase transition material at a critical temperature (τ_c) around 68 °C, accompanied by a reversible metal to insulator transition (MIT).^{1, 2} With regard to the pure VO₂, the insulating phase ($\tau_c < 68$ °C) with a monoclinic $P 2_1/c$ crystal system shows strong transmission at the infrared (IR)/near infrared (NIR) range, while the metallic counterpart ($\tau_c > 68$ °C) with a tetragonal $P 4_2/mnm$ crystal system exhibits depressed transmission across IR/NIR.^{3, 4} The thermal modulating abilities in IR/NIR and electrical conductivity contrast across τ_c make VO₂ a promising candidate in thermochromic smart window and various smart sensor applications.⁵⁻⁸ Especially for the smart window, the IR/NIR light can be transmitted ($\tau < \tau_c$) or absorbed ($\tau > \tau_c$) automatically according to the out-door temperature, maintaining the comfortable indoor environment, which meets the nowadays energy-saving requirements.⁹

However, the high τ_c , low visible transmission (T_{lum}) and the low solar modulating abilities (ΔT_{sol}) of pure VO₂ are three main drawbacks to be overcome.^{9, 10} Moreover, there is always a trade-off between enhancing both T_{lum} and ΔT_{sol} simultaneously.¹¹ With respect to τ_c , the extra strain energy¹² and doped by metal cations with large ion radii/large valence state¹³⁻¹⁵ have been proved to be effective in reducing τ_c . As for T_{lum} , the microroughness,¹⁶ widening band gap (E_g),¹⁷ biomimetic nanostructure,¹¹ nanogrid⁷ and porous morphology¹⁸⁻²¹ have been reported to be able to increase T_{lum} . Lastly, the ΔT_{sol} is always believed to be correlated to the solid contents of VO₂²² and/or surface plasmon resonance (SPR)^{10, 23} in some special surface/interface conditions.

Rare earth (RE) elements are characterized with large ion radii and abundant valence electrons, which always contribute to the enhancement of physical properties as dopants.²⁴⁻²⁶ Europium cation (Eu³⁺) has been found to be effective in reducing τ_c of VO₂ with a rate of -6.5 °C/at.%, and a moderate combination of T_{lum} =54%, ΔT_{sol} =6.7% was achieved.¹³ Terbium cation (Tb³⁺) was reported to be helpful in increasing the T_{lum} from ~45% to ~79%, but only a relative low τ_c reducing rate (-1.5 °C/at.%) could be obtained.²⁷ As predicted by Chao Sun et al. using the density functional theory (DFT) calculation,²⁸ the doping of lanthanum cation (La³⁺) could cause the V-V distance change and great V-V dimer distortion, which may result in a decrease of τ_c . In this paper, La³⁺ cations were firstly doped into VO₂ lattice at different doping

levels experimentally from 1 to 5 at.%. It was found that the τ_c of MIT could be reduced in a rate of -1.1 °C/at.% and a combination of T_{lum} =50%, ΔT_{sol} =10.3% could be achieved at the 4 at.% doping level.

Experimental section

All of the chemicals V₂O₅ (99.6%, Alfa Aesar), La₂O₃ (99.9%, Alfa Aesar and H₂O₂ (30 wt.%, Sigma-Aldrich) were used as received without any further purification.

Precursor preparation. 182 mg V₂O₅ and weighed La₂O₃ powder were added into 5 mL hot H₂O₂ (30 wt.%, 90 °C) solution under vigorous stirring. After a violent evaporation and cooling down to room temperature, another 15 mL H₂O₂ (30 wt.%) was added into the suspension, and a clear brown color precursor solution was attained after stirring for 4 minutes. Then the precursor was moved to do the dip coating at once. It should be noted that the reaction should be done in a 300 mL beaker due to the strong heat release during the reaction between V₂O₅ and hot H₂O₂.

VO₂ thin film fabrication. A fused silica substrate with the dimension 15×15×0.5 mm³ was dipped into the precursor solution at a rate 50 mm/min. After immersing for 20 seconds, the substrate was lifted up vertically at a withdrawing rate 200 mm/min. After drying in air, a brownish thin film with the thickness ~60 nm/side was got on the substrate. Then the thin film was moved into a tube furnace and annealed at 550 °C for 2h in an Ar flow (200 mL/min).

Characterization. The phase of the products was characterized with a Shimadzu XRD-6000 X-ray diffractometer (Cu-K α , λ = 0.15406 nm) using a voltage of 40 kV and a current of 30 mA at an X-ray grazing angle of 1.0°. Their morphology and La doping level were determined using a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan) with an INCA EDX detector at an accelerating voltage of 5 kV and 20 kV, respectively. For conventional transmission electron microscopy (TEM) studies, i.e., using selected area electron diffraction (SAED), bright field (BF) imaging, an JEOL 2010 (JEOL Company, Japan) microscope was used at an accelerating voltage of 200 kV. Transmittance spectra in the range 250-2500 nm were measured using a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) equipped with a Linkam PE120 system Peltier heating & cooling stage. The integrated visible transmittance (T_{lum} , 380-780 nm) and solar/IR transmittance (T_{sol} , 280-2500 nm; T_{IR} , 780-2500 nm) were calculated based on the recorded %T spectra using the expression

$$T_{lum/sol} = \int \phi_{lum/sol}(\lambda) T(\lambda) d\lambda / \int \phi_{lum/sol}(\lambda) d\lambda \quad (1)$$

where $T(\lambda)$ is the recorded film transmittance, ϕ_{lum} is the standard luminous efficiency function for the photopic vision of human eyes²⁹ and ϕ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).³⁰ The hysteresis loop of %T at a wavelength of 2000 nm was measured at temperatures ranging from 20 to 100 °C. In order to attain the phase transition temperature τ_c , the temperature-dependent heating and cooling %T(τ) data were fitted using a sigmoidal function of the form:³¹

$$\%T(\tau) = A2 + (A1 - A2) / [1 + \exp(\tau - \tau_c) / B] \quad (2)$$

where τ is the temperature in °C and $A1$, $A2$, τ_c and B are fitting parameters. Two phase transition temperatures $\tau_{c,h}$ and $\tau_{c,c}$ were obtained in the heating and cooling cycles, respectively and the average phase transition temperature was defined as $\tau_c = (\tau_{c,h} + \tau_{c,c}) / 2$, $\Delta \tau_c = \tau_{c,h} - \tau_{c,c}$. The solar modulating ability is termed as $\Delta T_{sol} = T_{sol}(20^\circ\text{C}) - T_{sol}(90^\circ\text{C})$.

Results and discussion

Synthesis of La doped VO₂ thin films

Figure 1a shows the XRD patterns of the pristine and La doped VO₂ thin films. The bump around 20° (2θ) in the XRD patterns should be ascribed to the diffraction of the amorphous fused silica substrates. All of the thin films exhibit the characteristic (011) XRD peak of VO₂ (monoclinic, $P 2_1/c$, JCPDS #82-661) around 28° (2θ), and no other impurity phase can be found, indicating the successful synthesis of VO₂ phase. Compared with the pristine VO₂, the (011) peak position in the 5 at.% La doped sample is left-shifted by 0.2° from 28.0° to 27.8°, which indicates the lattice expansion arising from the replacement of V by La with relatively larger ionic radius (1.032 Å v.s. 0.58 Å) in accord with the DFT calculation.²⁸ The La doping levels were further confirmed by EDX analysis with a 10% derivation. As depicted in Figure 1b, the EDX results agree well with the expected doping levels.

Fig. 1 (a) XRD patterns of the pristine and La doped (1-5 at.%) VO₂ thin films. (b) La doping levels determined by EDX characterization with a 10% derivation.

Figure 2 shows the morphology evolution of the pristine and La doped VO₂ thin films tested using FESEM. All of the samples show nanograin packed morphology, and the average grain size for the 0-5 at.% La doped samples is 61, 72, 84, 79, 62 and 73 nm, respectively, which shows that the La doping gives rise to a slight increase of the grain size. The roughness and thickness of the thin films have been detected using AFM under tapping mode, which have been tabulated in Table 1. The thickness of the La-doped samples shows a derivation compared to the pristine VO₂ thin film by $\sim \pm 14$ nm, while the roughness exhibits a slight increase by 1.1-5.6 nm. The TEM characterization of the 3 at.% La doped sample has been shown in Figure 3. As shown in Figure 3a-b, the bright-field TEM images reveal that the average grain size of the sample is

~ 80 nm, consistent with the SEM result (Figure 2). The SAED as shown in Figure 3c exhibits diffraction rings that can be indexed by (011), (200), (021) and (022) faces of VO₂, which indicates the polycrystalline nature of the La doped VO₂ thin film. The doping of La was further investigated through STEM. As shown in Figure 3d, the atom replacement of V by La could be clearly observed in the high resolution STEM image, where the La atoms with larger atomic number are brighter than the V atoms, arising from their different contributions to the elastic scattering signals collected by the detector. In addition, the STEM-EDX elemental mapping (Figure 3f) related to the view of HAADF (high angle annular dark field) shows that the La atoms are incorporated in the VO₂ lattice as the distribution of La signal matches the lattice plane arrangement.

Fig. 2 FESEM images for the pristine (a) and La doped (1-5 at.%, b-f) VO₂ thin films. The scale bar in the images is 500 nm.

Fig. 3 TEM (a) and the enlarged TEM image (b) of the 3 at.% La doped VO_2 grains. (c) SAED pattern of the polycrystalline 3 at.% La doped VO_2 grains. (d) STEM image of the 3 at.% La doped VO_2 grain. (e) HAADF image of the doped sample. (f) The La element mapping related to (e).

Thermochromic properties

Figure 4a shows the transmittance (%T) spectra ($250 < \lambda < 2500$ nm) of the samples at the temperature 20 and 90 °C, respectively. Upon heating from 20 to 90 °C, a large %T contrast in the IR range could be observed for all of the samples, which should be ascribed to the MIT.^{20, 32, 33} The integrated T_{lum} and ΔT_{sol} were tabulated in Table 1 and Figure 4b shows the doping level dependent average T_{lum} and ΔT_{sol} . It can be observed that the best combination of $T_{\text{lum}}=50.1\%$, $\Delta T_{\text{sol}}=10.3\%$ was achieved at the La doping level 4 at.%, which represents the best value for RE-doped VO_2 thin films,^{13, 27, 34} and is comparable to other doping cases without RE.³⁵⁻⁴⁰ It is of interest that both of average T_{lum} and ΔT_{sol} at the La doping level 5 at.% are higher than that of pristine VO_2 (69.2 %, 9.0 % v.s. 64.8%, 7.3 %), which should be due to a surface plasmon resonance peak around 1250 nm arising from the La doping. The %T hysteresis loop was

recorded at the wavelength 2000 nm in a temperature range 20-100 °C. As shown in Figure 4c, after doping with La, the MIT tends to move toward lower temperature until the doping level of 4 at.%, which is similar to the case of Eu doping.¹³ Plots of doping level dependent τ_c were shown in Figure 4d, and a τ_c reducing rate of -1.1 °C/at.% could be attained below the doping level of 4 at.%. This is the first experiment to prove the efficiency of La doping in reducing τ_c as indicated in simulation work using DFT calculation.²⁸ With respect to the τ_c reduction mechanism, besides the lattice distortion from the substitution of large La atoms calculated by DFT,²⁸ the increase of hole carrier density (h^+) from V^{5+} propagating caused by La doping ($\text{V}^{4+}_{1-2x}\text{V}^{5+}_x\text{La}^{3+}_x\text{O}_2$) should also contribute to the adjustment of τ_c .⁴¹ The competition between these two mechanisms should be the reason why τ_c starts to increase at higher La doping level.

Fig. 4 (a) UV-Vis-NIR spectra of the pristine and La doped (1-5 at.%) VO_2 thin films under the temperature 20 and 90 °C. (b) Average T_{lum} and the ΔT_{sol} of the VO_2 thin films with different La doping levels. (c) %T hysteresis loop of the pristine and La doped (1-5 at.%) VO_2 thin films. (d) Plots of τ_c v.s. La doping level.

As listed in Table 2, compared to other two reported rare earth dopants Eu^{3+} and Tb^{3+} , the La^{3+} cation has the largest ionic radius. The average T_{lum} of the RE-doped VO_2 thin films decrease with the ascending ionic radius of dopants and this is consistent with the fact that larger ions result in greater electronic polarization and slower velocity of light, leading to a larger refractive index. From Tb^{3+} to Eu^{3+} dopant, the ionic radius increases from 0.92 to 0.95 Å and the τ_c reducing rate is increased from 1.5 to 6.5 °C/at% which should be due to the larger lattice distortion. However, the largest size La^{3+} doping shows the lowest τ_c reducing rate and the reason remains unknown, but some dot defects in the form of La insertion in the seriously distorted lattice may be partially attributed to this phenomenon. In addition, compared to the previous reported W-/Mg-doped VO_2 continuous thin films (Table 2), the La-doped thin film shows the best combination of T_{lum} (50.1%) and ΔT_{sol} (10.3%).

Figure 5a shows the %A and %R spectra of the pristine and La doped VO_2 thin films. It can be found that the %A and %R could be changed by the La doping, where the 5 at.% and 4 at.% La doped

samples exhibit the lowest and highest %A / %R, resulting in their highest and lowest %T, respectively. In order to further investigate the La doping effects on the optical properties, the direct bandgap (E_g) of the VO_2 thin films was calculated by fitting the linear part of $(\alpha\hbar\omega)^2$ v.s. E curves (Figure 5b) based on the equation $(\alpha\hbar\omega)^2 = A(\hbar\omega - E_g)$,^{44, 45} where α is the absorption coefficient ($\alpha d = -\ln(T/1-R)$), A is a constant and $\hbar\omega$ is the photon energy. As depicted in the inset of Figure 5b, the E_g of the VO_2 thin films is gradually declined upon doping with La and the lowest value 2.42 eV is got at the doping level of 3 at.%, then it returns back with further doping. The decrease of E_g below the doping level 3 at.% is similar to the case under tungsten (W) doping arising from the larger ionic radius,⁴⁶ and the following E_g widening should be due to the competition between the effect of large ionic radius and h^+ carrier density. Since the change of band gap is of electronic nature,⁴⁴ the E_g narrowing of La doped VO_2 thin films below 3 at.% doping should be also related to the change of band structure resulted from the La doping in the lattice.

Fig. 5 (a) %A and %R spectra of the pristine and La doped (1-5 at.%) VO₂ thin films at room temperature. (b) Curve of $(\alpha\hbar\omega)^2$ v.s. E and the band gap E_g (inset) under different La doping levels.

Table 1. Thermochromic properties of the La doped VO₂ thin films.

Doping level/at.%	Thickness/nm	Ra ^a /nm	$T_{lum}(20^\circ\text{C}/90^\circ\text{C})/\%$	$\Delta T_{sol}^b/\%$	$\tau_c(\text{heating/cooling})/^\circ\text{C}$
0	74	3.0	64.8/64.8	7.3	79.9/57.1
1	83	4.4	61.1/61.3	9.1	76.1/52.4
2	60	8.6	67.5/67.7	6.2	79.6/54.2
3	72	4.4	55.8/56.6	8.4	76.2/54.9
4	90	4.1	49.9/50.4	10.3	75.9/49.2
5	80	5.5	69.5/68.9	9.0	80.2/55.2

^a Ra is the average roughness; ^b $\Delta T_{sol} = T_{sol}(20^\circ\text{C}) - T_{sol}(90^\circ\text{C})$.

Table 2. Doping effects on the thermochromic performance of VO₂ continuous films.

RE doping						
cation	Ionic Radius/Å	Doping /at.%	Ave. $T_{lum}/\%$	$\Delta T_{sol}/\%$	d τ_c /d at.%	Ref.
Eu ³⁺	0.95	4	54	6.7	-6.5	13
Tb ³⁺	0.92	4	65.9	4.6	-1.5	27
La ³⁺	1.03	4	50.1	10.3	-1.1	This work
Other dopings						
W ⁶⁺	0.6	2	45.1	6.9	20	42
Ti ⁴⁺	0.605	1	40	4.6	-	43
Mg ²⁺	0.72	5	82.1	4.8	1.4	10

Notes: The thickness, roughness and grain size of the RE-doped VO₂ thin films are at the same level.

Conclusions

In summary, a series of La doped VO₂ thin films were prepared through a facile sol-gel method, and the thin films exhibited high visible transmission and large solar modulating abilities. Especially, the 4 at.% La doped sample shows the best combination of T_{lum} =50.1% and ΔT_{sol} =10.3% compared with other reported VO₂ continuous thin films. Compared with pristine VO₂, 5 at.% La doped sample can increase T_{lum} and ΔT_{sol} simultaneously. La doping was firstly proved to be able to reduce the τ_c of MIT in experiment which is consistent with the simulation work, and it followed a reducing rate of -1.1 °C/at.% below the doping level of 4 at.%. A narrowing down of band gap was observed below the doping level of 3 at.%, which should be ascribed to the change of band structure caused by the doping in VO₂ lattice with large La atoms. This investigation of La doping effects on thermochromic properties of VO₂ thin films should be useful for other element doping researches with large ionic radius and low valence state.

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